PREPARATION AND CHARACTERISTICS OF NON-BLEEDING COCKTAIL CHERRIES DYED WITH CAROTENOID PIGMENTS

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SUMMARY

New means of dyeing cocktail cherries are needed because of possible restrictions in use of Red No. 3. A dyeing process which entails dehydration of cherries with ethanol, infiltration with an ethanolic solution of a red-colored carotenoid such as canthaxanthin, and then rehydration has been developed and patented by the Agricultural Research Service. An alternative process, not using ethanol as solvent, also has been developed. Such cherries will not bleed when heated in fruit cocktail, have an attractive red color, and retain their color for at least one year, if protected by addition of EDTA and storage in darkness.

INTRODUCTION

Cherries for fruit cocktail and fruit salad are artificially colored with a red dye that is made insoluble within the cherry tissue. Consequently, the dye cannot bleed into the syrup or fruit ingredients to give the product a pink hue. These "cocktail" cherries are prepared from sweet cherries that have been bleached and preserved in a strong calcium bisulfite brine. For many years, cocktail cherries were colored with FD&C Red No. 3, also known as erythrosine, a xanthine dye that could be infiltrated into the desulfited fruit as an alkaline solution and then precipitated by making the cherries acidic. In 1990, the U.S. Food & Drug Administration banned Red No. 3 for cosmetic uses and in lakes. Future action to ban Red No. 3 in cocktail cherries was expected.

As an alternative to Red No. 3, some producers of cocktail cherries have switched to carmine, the aluminum or calcium-aluminum lake of carminic acid. This colorant is solubilized with a dilute alkali and is then infused into the desulfited cherries. Various proprietary methods can be used to precipitate carmine within the cherry tissue so as to make the fruit non-bleeding. Carmine is derived from cochineal, the dried body of an insect, *Dactylopius coccus costa* (*Cossus cacti* L.) found in the Canary Islands and Peru. This colorant lacks Kosher certification, however, and is reputed to be expensive and difficult to use.

Our laboratory became involved in the development of an alternative colorant and dyeing method for cocktail cherries, largely because of some prior studies that we carried out in the 1970's with the red-colored carotenoid, canthaxanthin, and other red colorants for foods. At that time, FD&C Red Nos. 2 and 4 had been banned, and the safety of Red No. 40 was being questioned. We sought safe and stable water-soluble alternatives for use in maraschino cherries and other products. We found that aqueous dispersions of canthaxanthin, themselves optically clear, could not be used to dye cherries because of the inability of the pigment to penetrate into cherry flesh. However, some penetration did occur if the canthaxanthin was dissolved in ethanol rather than in water. This line of research appeared promising but was not pursued further when subsequent toxicological testing of Red No. 40 revealed no adverse effects, and concern about its safety diminished.

However, when the FDA's 1990 action against Red No. 3 created a need for alternative colorants for cocktail cherries, we realized that our earlier observations with canthaxanthin might be pertinent. Subsequently, we developed a unique process for dyeing cherries with carotenoids, and investigated the color characteristics and color stability of the experimental products. In today's presentation, I will review the results of these studies.

CHERRY DYEING PROCESS

Re-examination our earlier work with canthaxanthin suggested that the key to use of carotenoids as colorants for cherries was to make the aqueous cherry compatible with the water-insoluble pigment. This could be accomplished by displacing water in the fruit with ethanol *before* applying the ethanolic pigment solution so that diffusion of carotenoids through the cherry skin and flesh could occur. The insolubility of carotenoids in water, which interfered with dyeing in the earlier study, now could be used advantageously to make the cherries "non-bleeding." This could be accomplished by rehydrating the dyed fruit so that the pigments would precipitate within the cherry flesh and become immobile. Hence, our research efforts focussed on the development of a dyeing process based on these principles.

Desulfiting of brined cherries

As in other processes for coloring cherries, the first step was to remove sulfite from the fruit by leaching with cold or boiling water until the SO_2 residue was less than 100 ppm. Boiling appeared to cause some shriveling of cherry fruit during subsequent steps of the process but was faster and also decreased the extent of enzymatic browning that occurs when the sulfite level is reduced. The residual sulfite level did not appear critical with respect to color stability of the finished product.

Displacement of water in cherries with ethanol

Following desulfiting, the cherries were immersed in successive portions of ethanol, either 95% or absolute, and continuously stirred until the equilibrium ethanol concentration in the fruit exceeded 90%. This was determined by periodically measuring the specific gravity of ethanol samples, taken from the bulk ethanol-cherry mixture, with an alcohol hydrometer. The water displacement step was carried out at room temperature since use of hot ethanol produced some damage to the fruit, resulting in fragmentation. Insufficient water displacement resulted in precipitation of the carotenoid during dyeing.

Preparation of carotenoid dyeing solutions

Carotenoid solutions for cherry dyeing were prepared from three commercially available products: water-dispersible canthaxanthin from Roche; apo-carotenal, also from Roche; and oleoresin paprika from Meer. The structures of canthaxanthin, apo-carotenal, and capsanthin, the major carotenoid in paprika, are shown in Fig. 1.

Canthaxanthin solutions, containing 0.2% of the carotenoid, were prepared by dispersing the spray dried powder, which contains 10% canthaxanthin, in ethanol, with a Polytron homogenizer. The suspension was heated to the boiling point and then filtered through Whatman No. 541 paper under vacuum. The undissolved residue was re-extracted several times with boiling ethanol to remove residual canthaxanthin. All extracts were filtered and combined. Solutions containing 0.03% apo-carotenal or 0.5% oleoresin paprika were prepared by dissolving the colorants directly in ethanol without heating or filtering. Because of differences in tinctorial strength among the carotenoids used, these dyeing solutions differed widely in carotenoid concentration but imparted comparable color levels to the cherries, as judged visually.

Dyeing of cherries

Cherries that had been dehydrated in ethanol were drained, combined with the carotenoid solutions at a fruit to solution ratio between 1:1 and 1:2 (weight/volume), and mixed continuously at ambient temperature. Within 2-3 hours, the carotenoids penetrated through the skin and diffused throughout the cherry flesh. The spent ethanol could be recovered by distillation for recycling in the dehydration or dyeing steps of the process.

Rehydration of dyed cherries

Following the dyeing step, the cherries were drained and leached with cold water until their ethanol content was reduced below 3-4%. Residual ethanol would be lowered further to less than 0.1% by dilution when the cherries were added to fruit cocktail and allowed to equilibrate with the syrup and fruit. During rehydration, infused carotenoids precipitated and became "fixed" within the cherry flesh. Spent carotenoid solutions could be made up to strength for recycling.

The product

Experimental cocktail cherries, dyed with 0.2% canthaxanthin solution or 0.03% apo-carotenal solution, had an orange or tomato-red color, normal appearance and texture, and no off-flavors. Cherries dyed with canthaxanthin contained about 0.1% of this colorant, while cherries dyed with apo-carotenal contained less than 0.03% colorant, the lower level being used because of its greater tinctorial strength. Cherries dyed with oleoresin paprika had a less satisfactory color and slight paprika aroma.

Technology transfer - development of alternative process

The USDA cherry dyeing process was patented in 1991 (Sapers, 1991), and efforts were undertaken to commercialize the technology. While a number of companies showed interest in the process, and one company collaborated with the Agricultural Research Service in refining the technology under a Cooperative Research and Development Agreement, the process has not yet been licensed to industry. This is due in part to uncertainty about the regulatory status of Red No. 3, and also to the product color, which is more orange-red than the hue imparted by Red No. 3 or carmine. However, the most serious objection raised by potential users of the technology is the use of ethanol as solvent which entails a flammability hazard and also requires the user to conform to the tight controls required by alcohol tax regulations.

Therefore, we developed an alternative process for dyeing cherries with carotenoids that achieves the same result, without the use of ethanol; a non-flammable GRAS solvent is used instead. Cherries prepared by the alternative process are similar in color and performance to the cocktail cherries produced by our patented process and contain less than 0.5% residual solvent. Further information about the alternative process can be obtained from the Technology Transfer Coordinator at the Eastern Regional Research Center.

COLOR CHARACTERISTICS OF CHERRIES DYED WITH CAROTENOIDS

Color bleeding

The extent of bleeding in cherries dyed with carotenoids was evaluated by adding experimental cherries, cut in quarters, to canned fruit cocktail from which the commercially dyed cherry pieces had been removed (Sapers, 1993). The fruit cocktail was heated to 95°C and then slowly cooled to 40°C. The fruit pieces and syrup were examined for evidence of color migration from the experimental cherry pieces. No bleeding occurred with cherries dyed with canthaxanthin or apo-carotenal.

Color of conventional and experimental cherries

The color of maraschino and cocktail cherries is related to the spectral characteristics of the colorants used in dyeing (Sapers, 1993). Visible absorption maxima for the carotenoids and for Red No. 40, which is used in maraschino cherries, are at shorter wavelengths than absorption maxima for Red No. 3 or carmine (Table 1). The carotenoids give a more orange-red color to cherries, while Red No. 3 and carmine impart a more pink or violet hue.

The color of conventional and experimental cherries was evaluated by tristimulus colorimetry with a Byk Gardner spectrocolorimeter using the CIELab color scale. We also obtained spectral curves showing percent reflectance vs. wavelength from 380-720 nm. Cherries were placed directly over the aperture above the sample port for measurement. Four replicates were measured and automatically averaged for each sample.

A comparison of tristimulus parameters indicated that commercial cherries, packed by major processors, and experimental cherries, dyed with canthaxanthin and apo-carotenal, had similar values of "L*", an indication of color lightness (Table 2). Cherries dyed with oleoresin paprika were somewhat darker and less red than the other samples. The experimental cherries, dyed with canthaxanthin and apo-carotenal, had higher values of chroma and hue angle than the commercial cherries. This is due largely to the greater values of "b", an indication of more yellowness, in cherries containing carotenoids. The experimental cherries, dyed with canthaxanthin and apo-carotenal, showed less reflectance than the commercial cocktail cherries in the blue (460 nm) and blue-green (500 nm) regions of the visible spectrum but were similar in the red region (640 nm) (Table 3). The reflectance of cherries dyed with oleoresin paprika was much lower in the red region.

The tristimulus and spectral data (Tables 2 and 3) are consistent with the more orange- or tomato-red color of the experimental cherries. Whether or not this color would be acceptable to consumers should be determined in the context of the cherries' end use, i.e., in fruit cocktail, by packers of this product.

COLOR STABILITY OF CHERRIES DYED WITH CAROTENOIDS

Preliminary studies suggested that the color stability of cherries dyed with canthaxanthin was excellent while cherries dyed with apo-carotenal tended to fade. To confirm these observations, we carried out more detailed storage studies in which the cherries were packed in a sucrose syrup or various preservative solutions (Sapers, 1993). The cherries were stored in air at 20°C, and monitored during storage by tristimulus colorimetry. Preservative solutions contained acetic or citric acid as an acidulant, benzoic acid as an anti-microbial agent, ascorbic acid as an antioxidant, and EDTA as a chelating agent to retard discoloration (Table 4).

Cherries dyed with apo-carotenal

Because of the possible involvement of metal ions in fading of apo-carotenal-dyed cherries, the first storage study was a comparison of cherries that had been desulfited and rehydrated in rusted steel containers or in glass and plastic containers. All other steps in the process were carried out in glass containers. The dyed cherries were packed in a preservative solution containing vinegar and benzoate, with or without added ascorbic acid and EDTA. All samples showed rapid fading and a shift in color from red to orange or yellow, as indicated by the increase in "L*", increase in hue angle, and decrease in reflectance at 640 nm (Fig. 2). Cherries exposed to metal containers showed greater initial change than cherries exposed to glass and plastic, but by 15 weeks, these samples were similar. Addition of ascorbic acid and EDTA to the preservative solution diminished but did not eliminate the destabilizing effect of metal exposure. This experiment demonstrated the need to exclude all sources of metal contamination and to add antioxidants and/or chelating agents to improve color stability.

In a follow-up study, apo-carotenal-dyed cherries were prepared without exposure to metal and packed in syrup or preservative solutions. Cherries packed in vinegar + benzoate or syrup showed substantial change in the tristimulus parameters and reflectance at 640 nm over 51 weeks at 20°C (Fig. 3). One of the samples was prepared with cherries that intentionally had not been adequately rehydrated following dyeing, so that the final product, in preservative solution, contained 12% residual ethanol, a defect that might be encountered in a poorly controlled dyeing process. This product showed more rapid color loss than any of the other treatments in the experiment. The color of properly prepared cherries could be stabilized for at least one year by adding both ascorbic acid and EDTA to the preservative solution. The combination of citric acid and ascorbic acid was almost as effective. These compounds were only partially effective when used individually.

During storage, cherries packed in preservative solutions containing ascorbic acid, or combinations of ascorbic acid with EDTA or citric acid, became more fragile than the other cherry samples. The cause of this defect, which appeared to involve a weakening of the cherry skin, is not known.

<u>Cherries dyed with canthaxanthin</u>

The color of cherries, dyed with canthaxanthin and packed in syrup or a preservative solution (Fig. 4), was much more stable than the color of cherries dyed with apo-carotenal (Fig. 3). This is evident in the small changes seen in tristimulus and reflectance measurements over one year of storage. Slightly better color retention was obtained with cherries packed in preservative solutions containing EDTA. The excellent color stability of cherries dyed with canthaxanthin is consistent with its reported stability in a number of food products.

During storage, cherries packed in vinegar + benzoate with added ascorbic acid appeared to darken slightly, although no parallel change in the tristimulus or spectral data was seen. Such darkening may be an indication of the nonenzymatic browning of dehydro-ascorbic acid, generated by oxidation of added ascorbic acid during storage. If necessary, this discoloration might be avoided by reducing the headspace volume or by vacuum packing. As was the case with apo-carotenal-dyed cherries, the presence of ascorbic acid in the preservative solution tended to increase cherry fragility.

Oleoresin paprika

Controlled storage studies were not carried out with cherries dyed with oleoresin paprika. However, we observed extensive fading in a sample prepared for color evaluation after several months at 4°C, presumably due to carotenoid oxidation. Because of the excellent results obtained with canthaxanthin, use of oleoresin paprika was not pursued further.

CONCLUSIONS

This study has demonstrated that non-bleeding cocktail cherries can be prepared with a carotenoid as colorant. A cherry dyeing process using ethanol as the colorant solvent has been developed and patented. An alternative version of the dyeing process does not use ethanol as the solvent.

The color of cherries dyed with carotenoids is more tomato-red than the color of conventional cocktail cherries.

The cherry color is stable for at least one year at ambient temperature if canthaxanthin is used as colorant. Apo-carotenal is less stable. However, the color stability of cherries dyed with apo-carotenal can be greatly improved by addition of EDTA to the solution in which cherries are packed.

The future use of carotenoids to color cherries will depend on FDA action concerning FD&C dyes and the economics of the process.

REFERENCES

Sapers, G. M. 1991. Process for manufacture of non-bleeding maraschino cherries. U.S. patent 5,019,405.

Sapers, G. M. 1993. Color characteristics and stability of non-bleeding cocktail cherries dyed with carotenoid pigments. J. Food Science. In press.

Table 1. Visible Absorption Maxima of Cherry Colorants

Colorant	Chemical Class	Solvent	Absorption λ Max (nm)	Visually Perceived Color
Red No. 3 (Erythrosine)	Xanthine	0.05% $NaHCO_3$	526	Purple-red
Red No. 40 (Allura Red)	Monoazo	Water	504	Red
Carmine	Hydroxyanthroquinone	Water	516,552	Purple, violet-red
Canthaxanthin	Carotenoid	Ethanol	466	Orange-red
Apo-carotenal	Carotenoid	Ethanol	488	Orange-red
Oleoresin paprika	Carotenoid	Ethanol	454,474	Yellow-orange-red

Table 2. Tristimulus Colorimetry of Commercially Dyed and Experimental Cherries

Product	Colorant	Tristimulus Parameter[a]		
		L*	Chroma[b]	Hue Angle[c]
Commercial				
Maraschino	Red No. 40	31.0	31.0	25.9
Cocktail (Product A)	Red No. 3	36.6	36.1	14.4
Cocktail (Product B)	Carmine	33.7	28.2	24.8
Cocktail (Product C)	Carmine	39.1	29.4	22.8
Experimental				
Cocktail	Canthaxanthin	35.0	45.4	42.1
Cocktail	Apo-carotenol	37.5	40.6	40.2
Cocktail	Oleoresin paprika	29.3	27.5	36.6

[a]CIELAB coordinates L^*, a^*, and b^*, measured with spectrocolorimeter.

[b]Chroma = $(a^{*2} + b^{*2})^{1/2}$.

[c]Hue Angle = $\tan^{-1} b^*/a^*$.

Table 4. Composition of Preservative Solutions for Storage Study

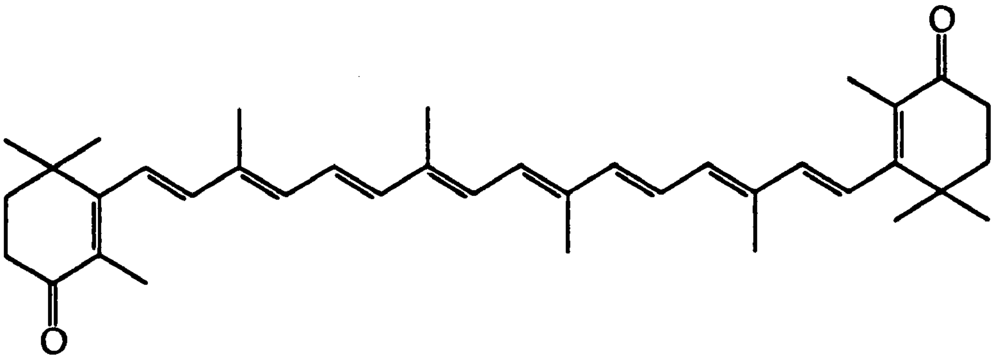
	Percent (W/V)						
Formulation	Acetic Acid	Benzoic Acid	Citric Acid	Ascorbic Acid	EDTA	$CaCl_2$	Sucrose
1	3	0.4	-	-	-	-	-
2	3	0.4	0.1	-	-	-	-
3	3	0.4	-	0.05	-	-	-
4	3	0.4	-	-	0.03	-	-
5	3	0.4	0.1	0.005	-	-	-
6	3	0.4	-	0.05	0.03	-	-
7	3	0.4	-	-	-	0.2	-
8	-	0.4	1	-	-	-	-
9	-	0.4	1	0.05	-	-	-
10	-	0.4	0.3	-	-	-	10

Table 3. Reflectance Spectra of Commercially Dyed and Experimental Cherries

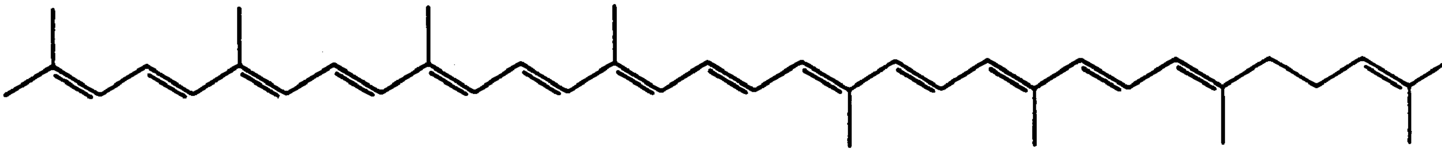
		Reflectance, Spectral Percent			
Product	Colorant	460 nm (Blue)	500 nm (Blue-Green)	540 nm (Yellow-Green)	640 (Red)
Commercial					
Maraschino	Red No. 40	3.7	3.4	3.6	22.2
Cocktail (Product A)	Red No. 3	6.7	4.0	3.1	25.
Cocktail (Product B)	Carmine	4.9	4.2	4.8	20.2
Cocktail (Product C)	Carmine	7.2	6.0	6.7	26.
Experimental					
Cocktail	Canthaxanthin	2.3	2.3	3.0	27.0
Cocktail	Apo-carotenol	3.6	3.6	4.5	29.
Cocktail	Oleoresin paprika	2.9	2.8	3.0	15.0

Fig. 1.

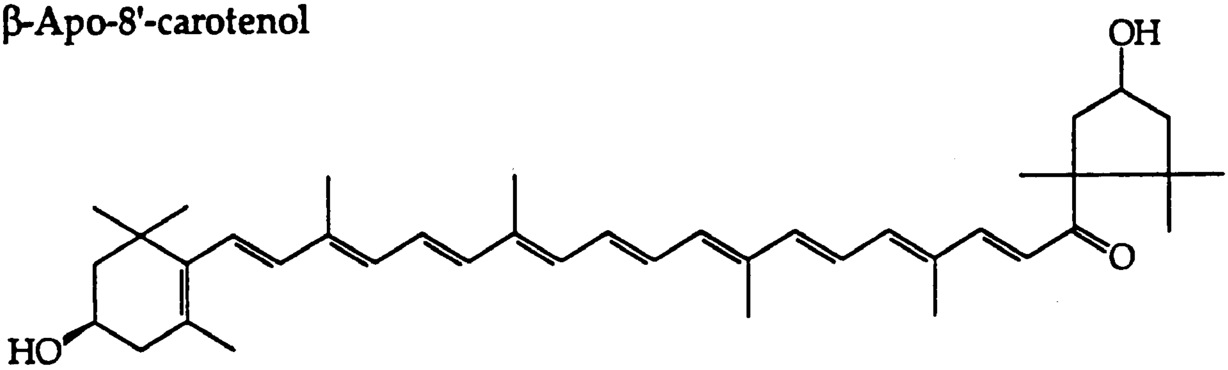
Structures of Carotenoid Colorants



Canthaxanthin



β-Apo-8'-carotenol



Capsanthin

Fig. 2. Color stability of cocktail cherries, processed in metal or glass containers, dyed with apo-carotenal, and stored at 20°C in dark.

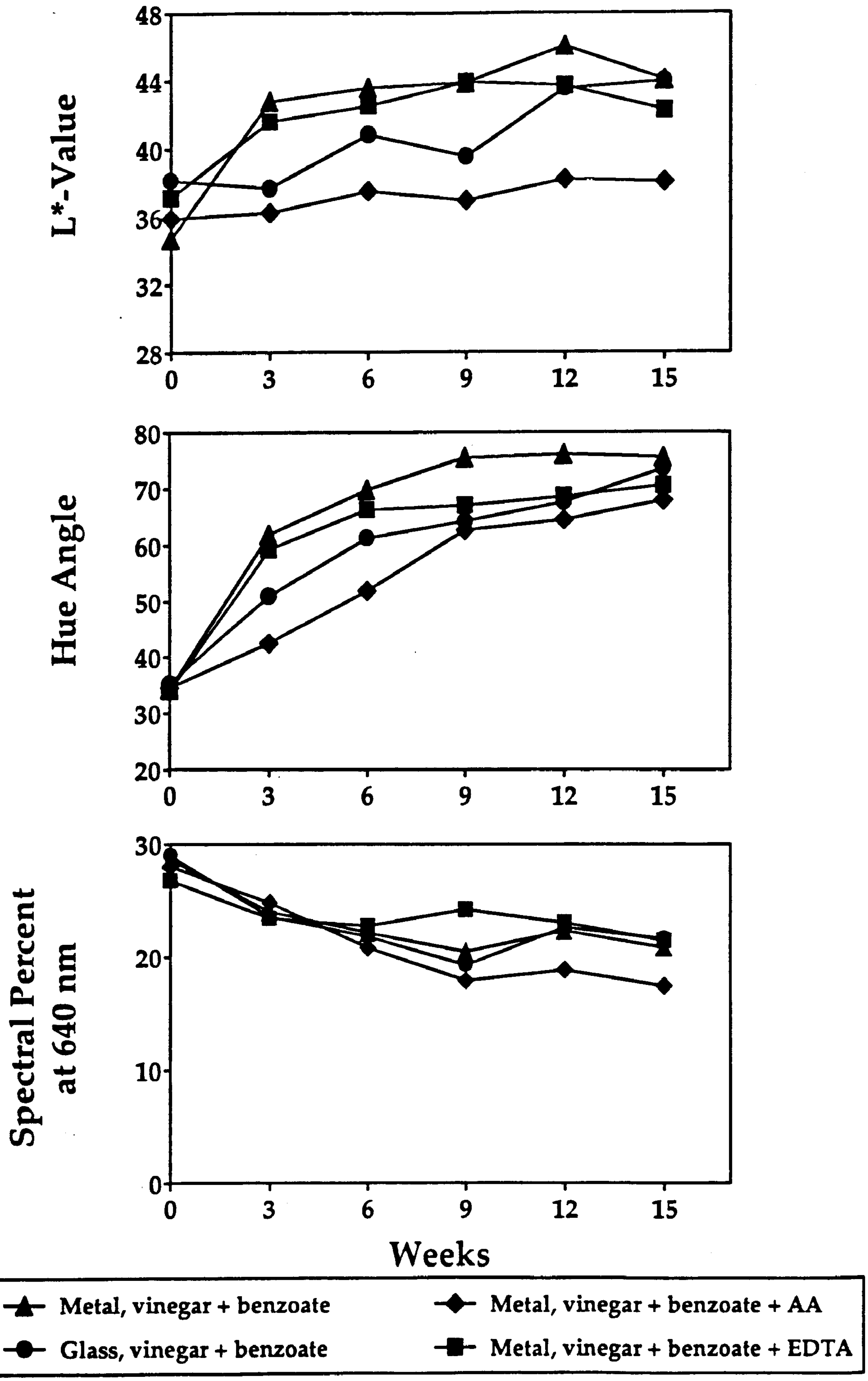


Fig. 3. Color stability of cocktail cherries, dyed with apo-carotenal, and stored at 20°C in dark in syrup or preservative solutions.

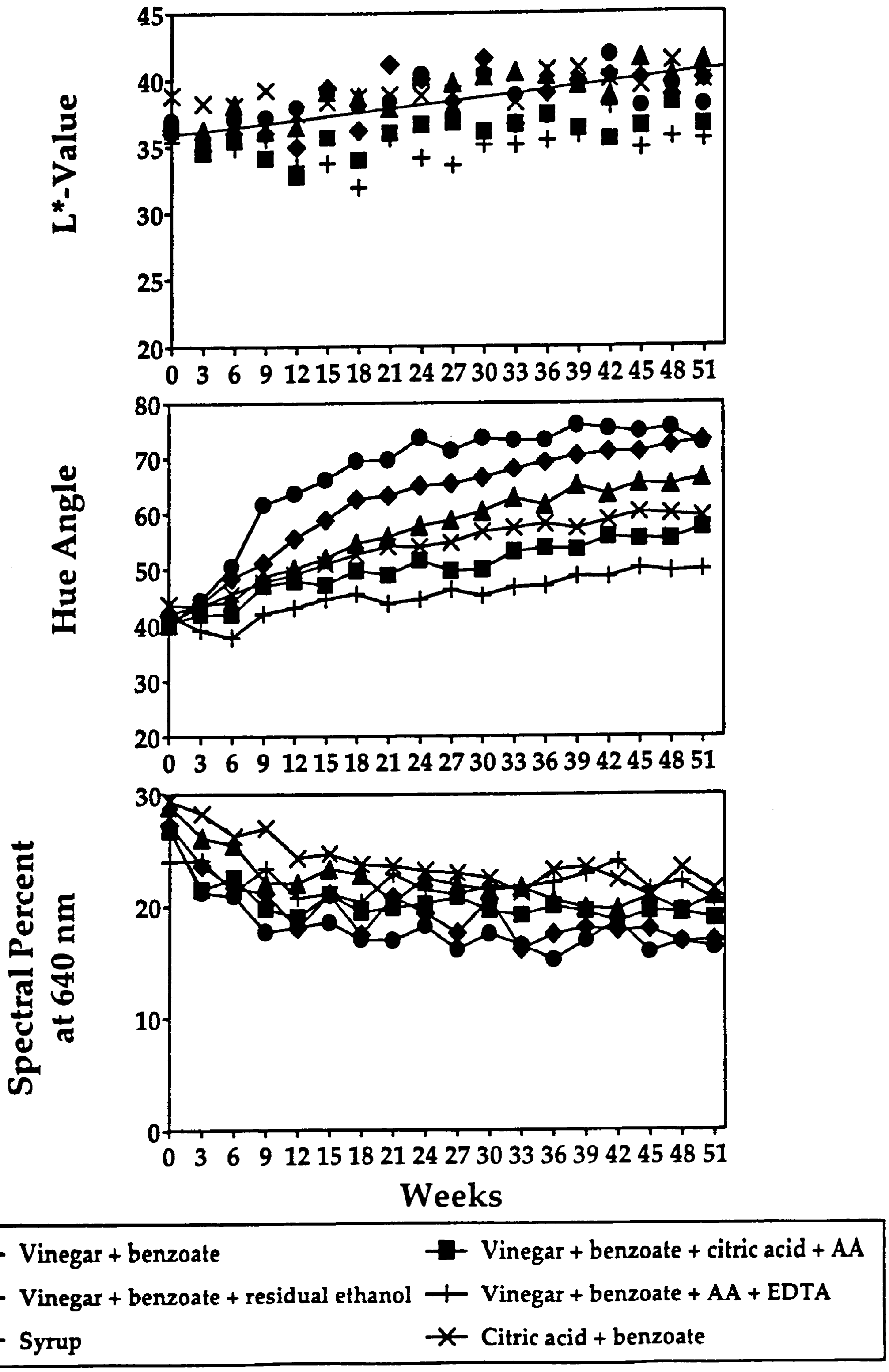


Fig. 4. Color stability of cocktail cherries, dyed with canthaxanthin, and stored at 20°C in dark in syrup or preservative solutions.